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AUTHOR(S):

Kumagai, Tetsu; Fujino, Osamu; Matsui, Masakazu; Shigematsu, Tsunenobu

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Coprecipitation of Cadmium with Aragonite

Tetsu KUMAGAI, Osamu FUJINO, Masakazu MATSUI,
and Tsunenobu SHIGEMATSU*

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The Coprecipitation behavior of cadmium during the precipitation of aragonite from calcium bicarbonate solution was investigated at 25°C. The distribution coefficient of cadmium between aragonite and solution phase increased with increasing concentration of magnesium chloride. This increment in distribution coefficient was caused by the increase of the ionic strength in the solution phase. The true distribution coefficient of cadmium is nearly independent of the concentrations of chloride and magnesium ions at a constant ionic strength, and is found to be 44 at 0.5 of ionic strength.

INTRODUCTION

Trace metals in marine organisms have become a significant topic of concern[1,2] because of direct and indirect impacts on human body through accumulations of metals in the food chain, but the informations on the distribution behavior of trace metals between shellfish and shell in marine bivalves are very few. Coprecipitation behavior of trace metals with calcium carbonate interested us as an essential phenomenon in distributing the metals into mineral shell.

There are some literatures dealing with the coprecipitation of trace metals with calcium carbonate,[3~9] because the distribution of trace elements in carbonate sediments could indicate the environmental conditions for the formation of the carbonate sediments.

In the present paper we are reporting the results of a series of experiments on the coprecipitation behavior of cadmium with aragonite.

EXPERIMENTAL

Reagents and apparatus used in the present experiment were almost the same as those described in the previous paper.[10]

Aragonite is precipitated from the calcium bicarbonate solutions containing magnesium chloride and trace cadmium by controlling the amount of magnesium chloride. The experimental procedures were also substantially the same as those which have previously been described.[11] The carrier and the radiotracer of cadmium and magnesium chloride were added to 0.01 M of the calcium bicarbonate solution in the thermostat. In the system keeping the ionic strength constant, appropriate amounts of magnesium perchlorate, sodium perchlorate and sodium chloride were also added to the bicarbonate solution. At appropriate intervals of time, an aliquot of the supernatant solution was pipetted out through a sintered glass filter. After

* 熊谷 哲, 藤野 治, 松井正和, 重松恒信 : Laboratory of Radiochemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

the centrifugal separation, calcium in the solution phase was determined by EDTA titration and cadmium was counted with a liquid scintillation spectrometer after 2 ml of 0.1 M hydrochloric acid and 15ml of liquid scintillator had been added to 2ml of the solution phase.

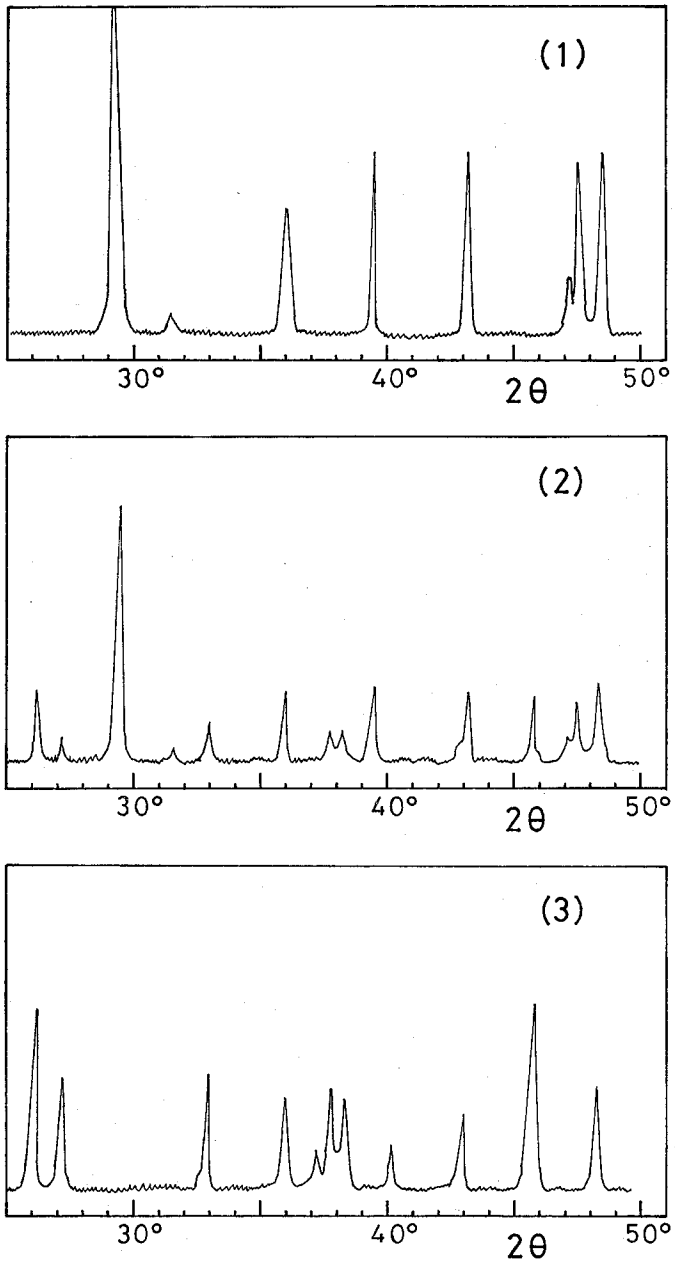

Fig. 1. X-ray diffraction patterns of calcium carbonate crystals. $MgCl_2$, (1), 0; (2), 0.00905 M; (3), 0.0233 M.

The homogeneous and logarithmic distribution coefficients, D[11,12] and λ[13] were calculated by means of the following equations:

$$D = \frac{C_{Ca} \cdot m_{CdCO_3}}{C_{Cd} \cdot m_{CaCO_3}} \quad (1)$$

$$\lambda = \log \frac{C_{Cd,\ initial}}{C_{Cd,\ final}} / \log \frac{C_{Ca,\ initial}}{C_{Ca,\ final}} \quad (2)$$

where C_{Ca} and C_{Cd} are the total concentration of calcium and cadmium ions in the solution phase. m_{CaCO_3} and m_{CdCO_3} are the mole fractions of calcium and cadmium in aragonite.

The formed carbonate precipitates were used for X-ray diffraction measurements of aragonite-calcite ratio. Samples of filtered crystals were washed with distilled water, dried and X-rayed with Ni-filtered Cu-K_α radiation with a Shimadzu X-ray Diffractometer, Model AZ-2A.

RESULTS AND DISCUSSION

Precipitates of Calcium Carbonate

The increase of magnesium ions in the mother fluid is advantageous for the formation of aragonite. Aragonite was precipitated from the calcium bicarbonate solutions containing more than 0.0233 M of magnesium chloride as shown in Fig. 1, where the ratio of the peak heights of the X-ray reflections (for example, aragonite 26.6°2θ/calcite 29.4°2θ) increased as the magnesium chloride contents increased. Magnesium ions in the aragonite precipitates could not be detected by atomic absorption spectrometry.

Precipitation Rate

Provided that the degree of supersaturation, S remains essentially constant during precipitation, the nonequilibrium distribution coefficient obtained experimentally, λ' is related to the apparent distribution coefficient, λ and the degree of supersaturation:[14]

$$\lambda' = \frac{\lambda S}{\lambda(S-1)+1} \quad (3)$$

The degree of supersaturation is directly related to the precipitation rate. Then, the influence of the precipitation rate on the distribution coefficient was examined by controlling the size of glass tubes through which carbon dioxide was gradually released from the bicarbonate solution.

The percentages of coprecipitated cadmium in the fraction of the aragonite precipitate at different inside diameters of glass tubes were plotted in Fig. 2. The experimental conditions are as follows: The concentrations of calcium bicarbonate, cadmium chloride and magnesium chloride were 0.01 M, 5×10^{-6} M, and 0.0274 M, respectively. The total volume of the reaction solution was 1.0 *l*, and the temperature was kept at 25°C. Precipitation rate was controlled by changing the vent

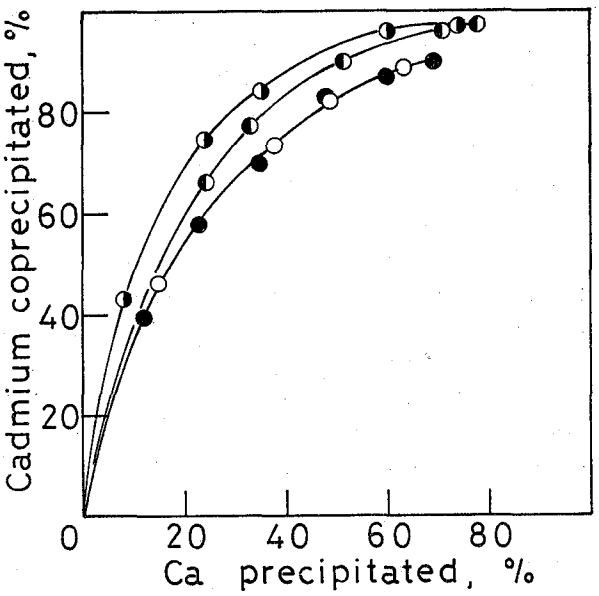

Fig. 2. The coprecipitation of cadmium with aragonite formed at various precipitation rates.
Ca^{2+}, 0.01M; Cd^{2+}, 5×10^{-6}M; $MgCl_2$, 0.027M; diameter of glass tube, ●, 2.5 mm ($t_{1/2}$=7.0 days); ○, 7.0 mm ($t_{1/2}$=5.0 days); ◐, 20 mm ($t_{1/2}$=1.8 days); ◑, openning of rubber stopper ($t_{1/2}$=0.8 day); temp., 25°C.

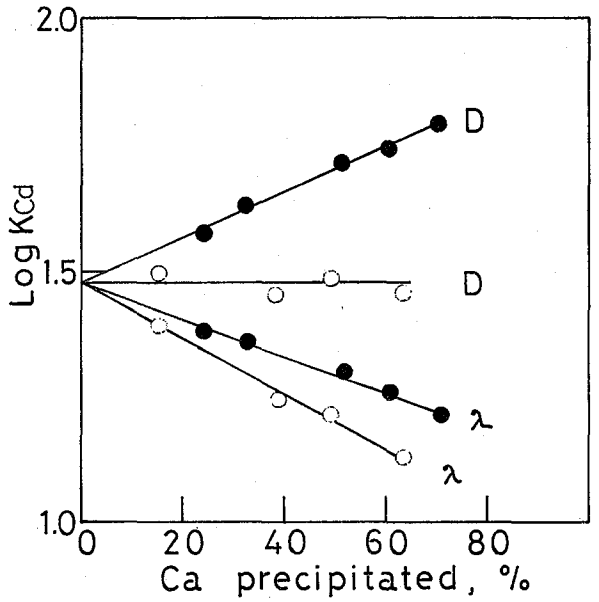

Fig. 3. The logarithmic and homogeneous distribution coefficients at each percentage of precipitated calcium.
$t_{1/2}$, ●, 1.8 days; ○, 5.0 days. Others are the same as in Fig. 1.

hole from 2.5 mm in diameter of the tube to the opening of the stopper. The time required to precipitate 50 per cent of calcium from the precipitation beginning, $t_{1/2}$ was 0.8 days when the stopper was open and $t_{1/2}$ was 1.8, 5.0, and 7.0 days when the diameter of the vent hole was 20.0, 7.0, and 2.5 mm, respectively.

The precipitation rate of aragonite became slower than that of calcite owing to such ion pair formation as $MgCO_3^0$. As shown in Fig. 2, the extent of the cadmium coprecipitation decreased as the precipitation rate decreased, but no change in the coprecipitation behavior was observed at slower rate than 5 days of $t_{1/2}$.

The logarithmic and homogeneous distribution coefficients, λ, and D, were calculated and plotted against the percentage of the calcium precipitation when $t_{1/2}=1.8$ and 5.0 days, as shown in Fig. 3. As illustrated in the figure, the nature of the coprecipitation process changed from logarithmic to homogeneous manner as the precipitation rate decreased, though the distribution coefficients extrapolated to zero per cent of calcium were nearly equal.

Effect of Magnesium Chloride

While keeping the other variables constant, aragonite was precipitated at the rate of $t_{1/2}=5.0$ days in the solutions containing 0.0233, 0.0468, and 0.0906 M of magnesium chloride. The effect was indicated in Fig. 4; the extent of the cadmium coprecipitation decreased as magnesium chloride increased. This is caused by the diminution of cadmium activity due to the complex formation of cadmium with chloride ions.

Cadmium ions form complexes and ion pairs with chloride ions in the solution

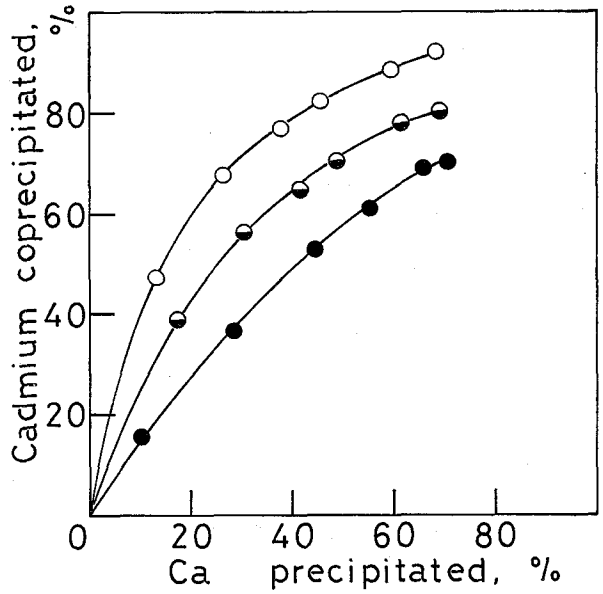

Fig. 4. The coprecipitation of cadmium at different concentrations of magnesium chloride.
$MgCl_2$, ○, 0.0233 M; ◒, 0.0468 M; ●, 0.0906 M; $t_{1/2}$, 5 days.

phase as follows, whereas calcium ions do not:

$$Cd^{2+}+nCl^{-} \rightleftarrows CdCl_n^{2-n} \qquad (4)$$

Then, the total concentration of cadmium is given by

$$C_{Cd} = m_{Cd}\{1+\sum \beta_i^{CdCl_i} m_{Cl}{}^i\} \qquad (5)$$

where m_{Cd} and m_{Cl} are the molar concentrations of cadmium and chloride, and $\beta_i^{CdCl_i}$ denotes the cumulative or gross stability constants of cadmium chloride.

As the concentration of chloride ions in the solution phase is extremely large as compared with that of cadmium dissolved in the solution, m_{Cl} is equal to the chloride concentration added to the solution as magnesium chloride. The relationship between the true distribution coefficient, D° and the apparent distribution coefficient, D′ is written as

$$D^0 = (1+\sum \beta_i^{CdCl_i} m_{Cl}{}^i)D' \qquad (6)$$

From the Eq. (6), the values of the true distribution coefficient, D^0 were calculated by the use of the calculated values of C_{Cd}/m_{Cd} in Eq. (5) and the observed values of the apparent distribution coefficient, D′. For the calculation above, the following values[15] of stability constant in the variable media of NaCl were adopted:

$$\beta_1^{CdCl} = 10^{1.76}, \quad \beta_2^{CdCl_2} = 10^{2.82}$$

The results were shown in Fig. 5, in which the true distribution coefficient was

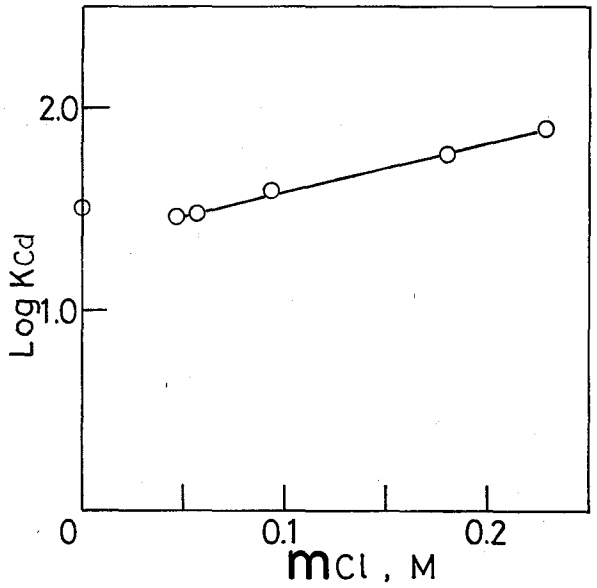

Fig. 5. The effect of chloride ions on the true distribution coefficient in magnesium chloride solution system.
0.025 M of $Mg(ClO_4)_2$ was used at $m_{Cl}=0$.

plotted against the concentration of chloride ions. The values of the true coefficient tended to increase with the chloride concentration.

Effect of Cadmium Concentration

The distribution coefficient is independent of the molar ratio of macro- and micro-components in the system forming the solid solution. To examine the effect of the molar ratio, the precipitation reaction was performed in the range of cadmium from 2×10^{-8} to 1×10^{-4} M. The results were shown in Fig. 6; there were no significant changes in the distribution coefficient except when the cadmium concentration is 2×10^{-8} M. The increment in the distribution coefficient at 2×10^{-8} M of cadmium may be caused by the adsorption of trace cadmium to the carbonate precipitates and the wall of the reaction vessel.

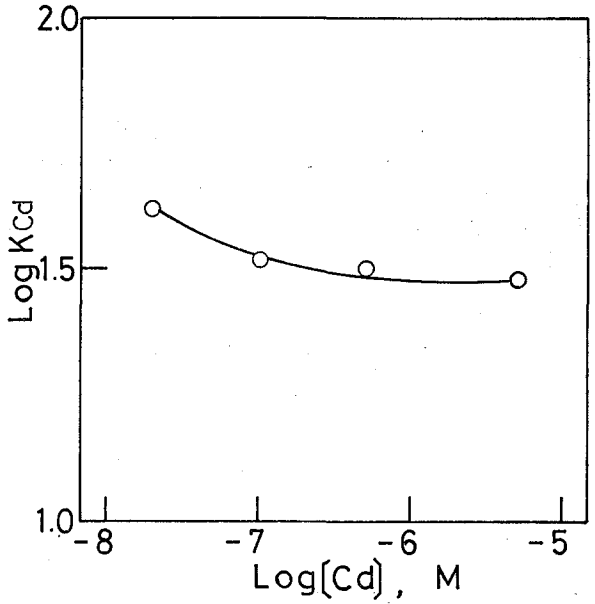

Fig. 6. The effect of cadmium concentration on the true distribution coefficient.

Constant Ionic Strength

In Fig. 5 the distribution coefficient of cadmium increased gradually with the increase of magnesium chloride. In this experiment, ionic strength in the solution phase underwent a change as the amount of magnesium chloride increased. Therefore, in order to examine whether the increment in the distribution coefficient in Fig. 5 is due to the variation of the ionic strength in the solution phase, the coprecipitation reaction was performed under the condition of a constant ionic strength, 0.5. Magnesium perchlorate was added to form aragonite, sodium chloride was used to change the chloride concentration, and sodium perchlorate was added to keep the ionic strength in the solution phase constant.

The coprecipitation was carried out in the solution containing 0.05, 0.10, and 0.20 M of chloride ions and containing 0.025 M of magnesium ions. The following values of stability constant[16] were adopted to calculate the true distribution coefficient, where the values were determined in the medium of $NaClO_4$.

$$\beta_1^{CdCl} = 10^{1.37}, \quad \beta_2^{CdCl_2} = 10^{1.80}$$

The results were shown in Fig. 7. The figure indicated that the homogeneous distribution coefficient, D in the solution of 0.1 M of sodium chloride was constant rather than the logarithmic one throughout the precipitation process. And the homogeneous distribution coefficient slightly increased as the coprecipitation reaction proceeded in the solution of 0.05 M of chloride, and the coefficient gradually decreased in the solution of 0.20 M of chloride. However, the distribution coefficient extrapolated to zero per cent of precipitated calcium gave a nearly constant value, $10^{1.64}$ *i.e.* 44, as shown in Fig. 8.

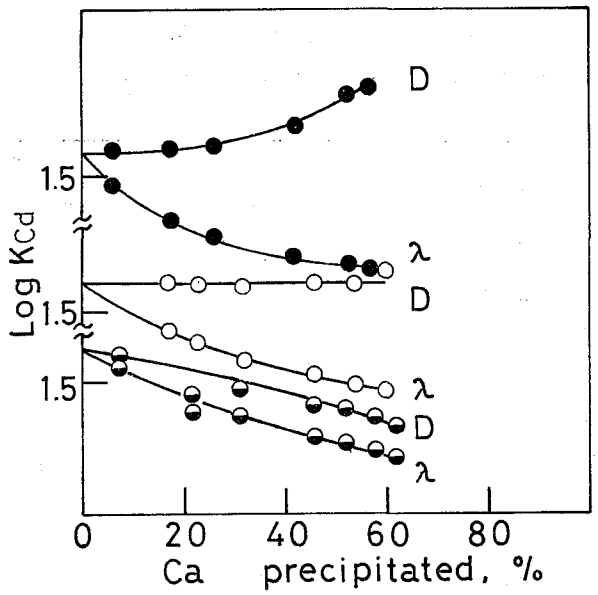

Fig. 7. The logarithmic and homogeneous distribution coefficients at a constant ionic strength.
NaCl, ●, 0.05 M; ○, 0.1 M; ◒, 0.2 M; ionic strength, 0.5; Mg^{2+}, 0.025M.

While keeping the other variables such as ionic strength and chloride concentration constant, the effect of magnesium ions in the coprecipitation system was examined in the range of magnesium ions from 0.1 M to 0.025 M. As shown in Fig. 9, the distribution coefficient of cadmium showed a nearly constant value. But strictly speaking, it tended to increase slightly as the magnesium concentration decreased. This may be due to the formation of trace calcite which has a large distribution coefficient.

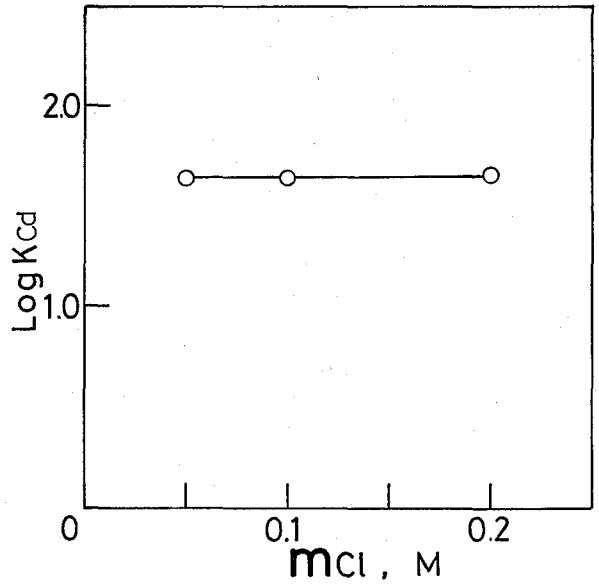

Fig. 8. The effect of chloride concentration at a constant ionic strength.

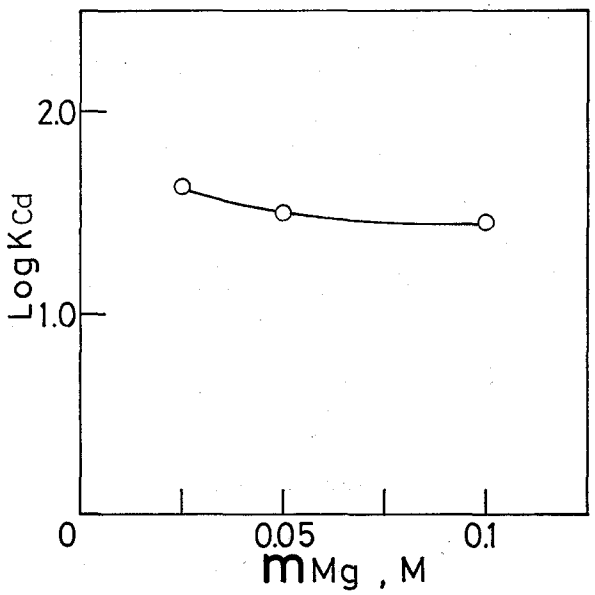

Fig. 9. The effect of magnesium ions at constant chloride ions.
Cl^-, 0.05 M; ionic strength, 0.5.

The increment in the distribution coefficient in Fig. 5 is undoubtedly caused by the change of the ionic strength in the solution phase rather than by the magnesium concentration and other factors.

The ratio of the solubility product constant of hexagonal cadmium carbonate to that of aragonite is 1350. The calculated value is considerably greater than the

value of the distribution coefficient measured experimentally, 44. This may be caused by the cadmium carbonate-aragonite structural difference (hexagonal-orthorhombic).

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